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APPLICATION NUMBER: 60/532,742

FILING DATE: *December 24, 2003*

RELATED PCT APPLICATION NUMBER: PCT/US04/43718

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)

Given Name (first and middle [if any]) Gary Dean	Family Name or Surname MARTINIE	Residence (City and either State or Foreign Country) 5616 Holly Street P.O. Box 11936 Dhahran 31311 Saudi Arabia
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 Additional inventors are being named on the _____ separately numbered sheets attached hereto.**TITLE OF THE INVENTION (280 characters max)**

REACTIVE EXTRACTION OF SULFUR COMPOUNDS FROM HYDROCARBON STREAM

Direct all correspondence to:

CORRESPONDENCE ADDRESS

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<input checked="" type="checkbox"/> Firm or Individual Name	ABELMAN, FRAYNE & SCHWAB Attorneys at Law		
Address	150 East 42 nd Street		
Address	New York, New York 10017		
City	State	Zip	
Country	U.S.A.	Telephone (212) 949-9022	Fax (212) 949-9190

ENCLOSED APPLICATION PARTS (check all that apply)

<input checked="" type="checkbox"/> Specification (includes drawings) Number of Pages	<input type="text" value="29"/>	<input type="checkbox"/> CD(s), Number	<input type="text"/>
<input type="checkbox"/> Drawing(s) Number of sheets	<input type="text"/>	<input type="checkbox"/> Other (specify)	<input type="text"/>
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76			

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)

<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	FILING FEE AMOUNT (\$)
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees	
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:	
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.	<input type="text" value="01-0035"/>
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

<input checked="" type="checkbox"/> No.	Docket Number:
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____	

Respectfully submitted,

SIGNATURE Jay S. Cinamon
TYPED or PRINTED NAME Jay S. Cinamon
TELEPHONE (212) 949-9022

Date	<input type="text" value="December 24, 2003"/>
REGISTRATION NO. (if appropriate)	<input type="text" value="24,156"/>
Docket Number:	<input type="text" value="206,399"/>

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Assistant Commissioner for Patents Alexandria, VA 22313-1450.

PROVISIONAL APPLICATION COVER SHEET**Additional Page**

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Docket Number	206,399	Type a plus sign (+) inside this box →	+
INVENTOR(S) APPLICANT(S)			
Given Name (first and middle (if any))	Family or Surname	Residence (City and either State or Foreign Country)	
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P.O. Box 1450
Alexandria, VA 22313-1450

Date: May 10, 2003

Inventor(s) Gary D. Martinie and Farhan M. Al-Shahrani
names: _____

Note to inventors: A patent is a document issued by a government entity. Documentation is essential before an idea is considered an invention by the government. An application filed without the needed information (e.g., prior arts, examples etc.) may be discarded by the patent office. The more relevant details one presents supporting the invention, the faster the application will be processed. Please include all related information including copies of publications, articles, and any related documents. All inventors identified in the application must have contributed to the invention.

Please contact an IAM team member if you have any questions or need help with the application. Please visit our website: <http://www.IAM.aramco.com.sa> regarding examples of patents and our contact information. *Please do not modify this document without contacting IAM. All starred (*) questions must be answered with sufficient details.*

- 1. Title of the invention:** Reactive Extractive Removal of Thioethers, Mercaptans, Disulfides, and Other Sulfur Species from Natural Gas, Liquefied Natural Gas, Natural Gas Liquids and Light Petroleum Fractions
- 2. *Summary of the invention:** This process is a new technology designed to remove thioethers, mercaptans, disulfides, and other sulfur species from NGL, which are not removed by other processes such as Merox. This process uses a liquid-liquid extraction of the hydrocarbon liquid phase with an aqueous phase containing a complex mixture of chemicals. The process involves reactive extractive technology using a water soluble cocktail of low-cost industrial chemicals to react with thioethers and other sulfur species to form chlorosulfonium ions, sulfenyl chlorides, sulfoxides, sulfones, sulfonic acids, sulfilimines, and other heavier, ionic, or water soluble species, and thereby separate and remove them from the hydrocarbon phase, trapping them in the aqueous phase. This process relies on the discovery of a new chemical reaction, the formation of sulfonium ions of thioethers and other sulfur species, in which the chlorine is added to the sulfur as the chloronium ion (Cl^+) as a result of action by chloronium agents including hypochlorites and chloramine species.
- 3. *Introduction and Background:**

(a) Introduction: The presence of sulfur compounds in petroleum arises primarily from incorporation of sulfur from the biomass that contributes to making petroleum. That is

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the sulfur in the kerogen, which is included as the petroleum molecules form by kerogen cracking under heat and pressure.

Hydrogen sulfide in natural gas can be formed by three means: the breakdown of labile sulfur containing molecules incorporated within the crude oil, the action of sulfur reducing bacteria present in the reservoir on the sulfur and carbon components in the petroleum, and by the thermo-chemical sulfate reduction (TSR) of anhydrite (calcium sulfate) found in some reservoirs. During TSR, the petroleum hydrocarbons react with sulfate to form hydrogen sulfide and carbon dioxide.

Carbon dioxide and hydrogen sulfide can react to form carbonyl sulfide, carbon disulfide, and water, and the reaction usually reaches an equilibrium depending on presence of water, carbon dioxide, hydrogen sulfide, and temperature and pressure.

Mercaptans react with oxygen to form disulfides and water, or they may react with iron oxide to give the same products. This reaction takes place rapidly with steel sample cylinders, which have iron oxide coating on the interior walls. Hence the use of titanium or other inert-walled sample cylinders.

Alkyl mono-sulfides like dimethyl sulfide are fairly inert, and non-polar. They have the polarity of propane. They do not react under most conditions. Dimethyl sulfide can be readily alkylated by methyl iodide, methyl sulfate, and other alkylating agents, and we have proposed this reaction in the 1990s as a possible new process. They may be also complexed by Lewis acids like cuprous bromide, boranes, mercuric iodide, zinc chloride, and iron chloride.

Sulfur compounds may be complexed by chloramines, such as Chloramine T and Chloramine B, forming new sulfur-amine bonds.

We have shown that DMS may be removed from butane or propane by three different molecular sieves: 13X, RK29, and RPG250 all available from UOP. The 13X molecular sieve has a high capacity for DMS and can be easily regenerated.

Saudi Aramco has discovered in 1994, the presence of dimethylsulfide in it's Marjan offshore gas field, and this compound is not removed by amine or Merox treatment. Present at around 5 ppm in the gas and liquids, the dimethylsulfide concentrates in the butane fraction where it can reach as high as two hundred ppm, and it varies from 10 to 200 ppm from time to time. Presence of Dimethylsulfide in butane causes a serious problem downstream, where butane is added to gasoline, burnt as a fuel in households, processed in Butamer units which use a platinum catalyst easily poisoned by only 1 ppm sulfur; Butane goes into the manufacture of Methyl t-Butyl Ether, and t-Butyl Hydroperoxide.

Dimethylsulfide is not usually found in NGL and hydrocarbon liquids, but when it occurs, can be very troublesome. Dimethylsulfide has been reported in NGL by others, for example, in a New Mexico Field by Texaco in 1995.

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As stated above, other sulfur species are also found frequently in butane, causing product quality problems, requiring that butane or propane product be flared, reinjected, reprocessed, or sold off at a discount. This may be due to process upsets, contamination, unreactive sulfur species that are not removed by Merox, corrosion, biological activity, or a myriad of other circumstances. These upsets and contaminations often result in great economic costs and expenditures, and interrupt the supplies of fuel and feedstocks, and cause the breaking of contracts and forfeiture of penalties and compensation.

(b) **Description of Invention:** This new process is a continuous liquid-liquid extraction of hydrocarbon liquid or liquefied hydrocarbon, or gaseous hydrocarbon, by a mixture of water soluble chemicals including Sodium Hypochlorite, Chloro, Dichloro, and Trichloro Isocyanuric Acid, and it's Sodium Salts, Sodium Hydroxide, Calcium Hypochlorite, Calcium Chloride, Calcium Perchlorate, and Calcium Carbonate. Each component is in the concentration range of 0-20 Weight %.

(c) **Describe any, unique, unexpected or unconventional features of it:** It is unexpected that this mixture of agents and some of the agents separately can complex and remove sulfur compounds from hydrocarbon streams. This process relies on the discovery of a new chemical reaction, the formation of sulfonium ions of thioethers and other sulfur species, in which the chlorine is added to the sulfur as the chloronium ion (Cl^+) as a result of action by chloronium agents including hypochlorites and chloramine species.

(d) **Provide a few key words related to your invention:** Sodium Hypochlorite, Hypochlorous Acid, Trichloroisocyanurate, losantin, cyanuric acid, sulfur compounds, hydrocarbons, reactive, extractive, desulfurize, sulfur, sulfur species, aqueous agent, aqueous solution, NGL, LNG, natural gas, liquified natural gas, natural gas liquids, light hydrocarbons.

.....
(e) Is your invention "obvious," clear or evident to those who are familiar with the area of your invention? Yes/no. Describe: No this invention is surprising, and wouldn't be expected by those familiar with this area of technology, and was developed as a result of innovative work, study, and experimentation.

4. *Previous work and literature related (or closely related) to your invention: (Please take as much space as needed to address any previous work as identified below)

(a) Have you reviewed what others have done in this area by reviewing the related papers or patents? **Explain.** Yes no We have carried out extensive reviews of patents and publications in this area, as evidenced by the following discussion of prior art.

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(b) Discuss any previous work, approach(s) or solutions(s); How do you propose to improve the current art or overcome the problems?

BACKGROUND ART

Removal of sulfur compounds from gas streams has been of considerable importance in the past and is even more so today due to environmental considerations. Gas effluent from the combustion of organic materials, such as coal, almost always contain sulfur compounds and sulfur removal processes have concentrated on removing hydrogen sulfide since it has been considered a significant health hazard and because it is corrosive, particularly when water is present. With increasing emphasis on eliminating or minimizing sulfur discharge to the atmosphere, attention is turning to the removal of other sulfur compounds from gas streams.

Numerous natural gas wells produce what is called in the industry "sour gas." "Sour gas" is natural gas that contains hydrogen sulfide, mercaptans, sulfides and disulfides in concentrations that make its use unacceptable. Considerable effort has been expended to find an effective and cost efficient means to remove these objectionable sulfur compounds from natural gas.

The removal of sulfur compounds and particularly chemically-combined sulfur, such as organosulfur compounds, from feedstreams is highly desirable for environmental concerns and in order to prevent potential catalyst deactivation as well as equipment corrosion.

Typically, hydrocarbon products contain various amounts of sulfur compounds in the form of, for example, chemically-combined sulfur, such as inorganically combined sulfur and organically combined sulfur, i.e., organosulfur compounds.

The presence of organosulfur compounds in hydrocarbon streams results naturally, as well as from the introduction of organosulfur compounds, into the hydrocarbon streams during conventional processes for producing and treating hydrocarbon products.

As previously indicated, if chemically-combined sulfur, such as organosulfur compounds, are not removed from the hydrocarbon streams, the presence of organosulfur compounds in the resultant hydrocarbon products, including natural gas, paraffins, olefins and aromatics, particularly gasoline or other fuels, can cause corrosion of processing equipment and engine parts, as well as other deleterious effects, particularly when water is present.

A number of processes are available for removal of H_{sub.2}S from natural gas streams. Processes presently available can be categorized as those based on physical absorption, solid adsorption, or chemical reaction. Physical absorption processes suffer from the fact that they frequently encounter difficulty in reaching the low concentrations of H_{sub.2}S required in the sweetened gas stream. Solid bed adsorption processes suffer from the fact that they are generally restricted to low concentrations of H_{sub.2}S in the

entering sour gas stream. Chemically reacting processes in general are able to meet sweet gas H_{sub.2}S concentrations with little difficulty, however, they suffer from the fact that a material that will react satisfactorily with H_{sub.2}S will also react with CO_{sub.2}. Above all, the processes presently available do not efficiently provide for removal of mercaptans, sulfides and disulfides.

An example of a chemically reactive process is the ferric oxide fixed bed process, wherein the reactive entity is ferric oxide impregnated on an inert carrier. This process is good for the removal of H_{sub.2}S but does not appreciably remove mercaptans or other sulfur compounds. The bed can be regenerated, however, the number of regenerations is limited by the build-up of elemental sulfur upon the bed.

A widely used process for removing H_{sub.2}S from natural gas depends upon the reactivity of H_{sub.2}S with amino nitrogen, see for example U.S. Pat. No. 1,783,901. In recent years several other patents have been granted covering similar compounds. The amine-like chemical compounds currently being employed for removal of H_{sub.2}S from gas streams include: monoethanolamine, 2-(2-aminoethoxy)ethanol and diethanolamine. While effective for removal of H_{sub.2}S, these compounds do not effectively remove mercaptans, sulfides or disulfides. Installation costs are high and operating costs are high due to substantial energy requirements.

The Shell Oil Company "Sulfinol" process involves both a physical solvent and a chemically reactive agent in the sweetening solution. The physical solvent involved is tetrahydrothiophene 1,1-dioxide and the amine is normally diisopropylamine. This process suffers from the disadvantage that the physical solvent has a high absorption capacity for the hydrocarbon gas constituents and the cost per unit is excessive.

In general, amine type sweetening processes tend to encounter the same kinds of operating problems, which can be roughly categorized as (a) solution loss, (b) foaming and (c) corrosion. In the presence of water H_{sub.2}S is corrosive, thus, elimination of corrosion in an amine sweetening unit is all but impossible because most amine type solvents are used in water solution.

Activated carbon and molecular sieves are well-known, however, absorption capacities are limited. Regeneration is possible but this requires sophisticated instrumentation and controls in addition to high energy requirements.

U.S. Pat. No. 4,035,474, KUNKEL et al., discloses a method for removal of sulfur from tail gas by use of a cold bed absorption process. This process utilizes a catalyst, however, catalyst deactivation occurs after 18 hours and a backup unit must be brought on stream while the spent catalyst is regenerated for 12 to 14 hours at 700.degree. F./370.degree. C.

The reaction of alkali metal salts of sulfonamides with sulfur compounds is known. For example, a kinetic study of the reaction between sulfides and N-sodium-N-chloro-paratoluene sulfonamide is reported in the Bull. Chemical Society Japan, V.42, 2631 (1969), K. Tsujihara, et al. From the mechanistic study of this reaction, a procedure for the synthesis of sulfilimines was devised.

A procedure is disclosed in U.S. Pat. No. 3,756,976, URANECK et al., which removes objectionable thiol odor from polymer latex through the use of numerous compounds that convert the odorous sulfur compounds to a nonodorous form. Specifically claimed is the use of the alkali metal salts of N-halogenated arylsulfonamides. U.S. Pat. No. 3,756,976 teaches the use of these compounds to convert the sulfur compounds to a nonodorous form and not the removal thereof. The disclosed process has the converted sulfur compounds within the polymer latex system and does not teach or suggest that sulfur compounds can be removed from a gas stream through use of the alkali metal salts of N-halogenated sulfonamides.

The reaction of sulfides with salts of N-chloroarenesulfonamides was the first method to be discovered for preparing sulfilimines. Gilchrist et al, Chem. Rev., Vol. 77, No. 3, page 409, 1977.

The reaction of Chloramine-T (trade name for N-sodium-N-chloro paratoluene sulfonamide) with thiols, disulfides, sulfides, sulfoxides and sulfones was reported by D. K. Padma et al, in Int. J. Sulfur Chem., Part A 1971, 1(4), 243-50 and titrimetric determination of mercaptans with chloramine-T is reported by R. C. Paul et al, in Talanta, 1975, 22(3), 311-12. All the references cited do not suggest or disclose that salts of sulfonamides such as chloramine-T can be used to remove sulfur compounds from a gas stream.

U.S. Pat. No. 4,283,373, FRECH et al., is directed to a method of removing sulfur compounds from a gas stream by contacting the stream with alkali metal salts of sulfonamides. The preferred sulfonamide disclosed is chloramine-T which can be sprayed into the gas stream, or the gas can be passed through a porous carrier impregnated with the chloramine, or through a resin with pendant substituted sulfonamide groups.

U.S. Pat. No. 3,306,945, CONVISER, is directed to a process for purifying liquid unsaturated hydrocarbons by removing impurities using molecular sieve materials. CONVISER discloses that sulfides (R-S-R), which include dialkyl sulfides, may be adsorbed by zeolitic molecular sieves material having sufficiently large pores to such impurities, such as the synthetic type X.

U.S. Pat. No. 4,592,892, EBERLY, Jr., is directed to a process of using a sorbent catalyst to remove sulfur from naphtha. The sulfur impurities which are disclosed as being removed are mercaptans, thiophenes, disulfides, thioethers, hydrogen sulfide, carbonyl sulfide, and the like; and the adsorbent is disclosed as a Group VI B and/or Group VIII metal catalyst, for example, cobalt molybdate or nickel molybdate supported on alumina.

U.S. Pat. No. 3,367,862, MASON et al., is directed to a process for desulphurizing heavy residual fractions by contacting with water in the presence of the catalyst comprising the metal, metal oxide, or metal sulfide, distended on a charred base.

Naphthas, which are used for reforming, typically contain between 50 wppm to 500 wppm sulfur as mercaptans, such as 2-propyl mercaptan, butyl mercaptan, and

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thiophene, hindered thiophenes, such as 2, 5-dimethylthiophene. Accordingly, naphthas for reforming are usually treated with hydrogen over a hydrotreating catalyst, such as a sulfided cobalt and molybdenum on alumina support, or nickel and molybdenum on alumina support, to protect reforming catalysts. Hydrotreating converts sulfur compounds to hydrogen sulfide, decomposes nitrogen and oxygen compounds and saturates olefins. Hydrotreating is done at a temperature between about 400.degree. F. and 900.degree. F., a pressure between 200 psig and 750 psig, liquid hourly space velocity between 1 and 5, and hydrogen circulation rate of 500 to 3000 scf/hr. Modern hydrotreating processes can reduce sulfur concentration in naphtha to 0.25 wppm and even to 0.1 wppm.

U.S. Pat. No. 3,898,153 is directed to purifying reformer feedstreams by passing hydrotreated reformer feedstock through a zinc oxide bed.

U.S. Pat. No. 4,634,518 passes hydrotreated reformer feed over massive nickel catalysts.

Other treatments for purifying hydrotreated feedstock for reforming are disclosed in U.S. Pat. Nos. 4,320,220; 4,225,417; 4,575,415; and 4,534,943; wherein the disclosed treatment is over manganese oxides.

A suitable manganese oxide formulation for this purpose which is commercially available is Sulfur Guard HRD-264 sold by Englehard wherein recommended treatment conditions are temperatures within the range of 600.degree. F. to 1000.degree. F., pressures within the range of about 150 psig to 700 psig, 1/1 to 30/1 hydrogen to oil molar ratio, and 500 to 50,000 gHSV.

U.S. Pat. No. 4,456,527 is directed to purifying hydrotreated feed for reforming over zeolite L catalysts.

U.S. Pat. No. 5,167,797 by John D. Y. Ou assigned to Exxon Claims a process for removal of sulfur contaminants from hydrocarbons using processes which rely upon the reaction of organosulfur compounds with N-halogeno compounds. The sulfur removal may be effected by using liquid/liquid extraction processes or one of two reactive adsorption processes involving injecting a stoichiometric amount of N-halogeno compounds into hydrocarbon and then passing the stream through an adsorbent column to adsorb the N-halogeno-sulfur compounds and any unreacted N-halogeno compounds; or using adsorbents which are pre-loaded with N-halogeno compounds which are placed in a fixed-bed column for sulfur removal.

German Patent No. 3 527 110-A, CIBA GEIGY AG, is directed to removing hydrogen sulfide from gases by oxidation using a solution containing anthraquinone sulphonamide and variable valency metal compounds followed by reoxidation, preferably using oxygen of hydroquinone.

The process is disclosed as being useful to purify gas, town gas, waste gases, and CO₂ rich streams from coal combustion, wherein the impurities which may be present are identified as including certain oxides of C, N and S, H₂, organic S compounds, and HCN.

British Patent No. 2 209 386, CIBA GEIGY AG, is directed to the removal of hydrogen sulphide from gases or liquid hydrocarbons by washing with alkaline solution containing anthraquinone disulphonamides. It is disclosed that hydrogen sulfide in gases is adsorbed, for subsequent removal in sulfur, by washing the gas with an aqueous alkaline solution of one or more anthraquinone sulphonamides.

European Application No. 74 894, CIE FRANCAISE RAFFINAGE, is directed to the extraction of hydrogen sulfide, carbon dioxide and the like, from hydrocarbon gases using sulphonamide or sulphamide as solvent. It is disclosed that undesirable gases, for example, H_{sub}2 S, CO_{sub}2, COS, and mercaptans, are removed from their mixtures with hydrocarbons and/or H_{sub}2 by a solvent whose molecule contains at least one group N--SO_{sub}2, and preferably a sulphonamide or sulphamide.

(c) How does your invention compare with those presented by other patents or publications? Please summarize previous related work.

Our invention uses a different process and different agents to accomplish the removal of sulfur species. These agents are more effective, more available, more compatible, and easier to use than other agents. Our agents and process are stabilized and regenerative, and when exhausted may be disposed of as biocides in wastewater, injection water, or be disposed to seawater.

(d) What are the deficiencies of the prior methods or approach(s)? Please compare.

Other processes fail to remove dimethylsulfide and disulfides, other thioethers. Other processes use expensive and unstable agents and chemicals. Other agents may be toxic or dangerous to dispose of.

5. *List summarize all previous work or references (related patents and publications, attach hard copies if available).

U.S. Patent Documents

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<u>2176196</u>	Oct., 1939	Beamer et al.	423/234.
<u>2181433</u>	Nov., 1939	Jordon	423/231.
<u>3306945</u>	Feb., 1967	Conviser	208/310.
<u>3367862</u>	Feb., 1968	Mason et al.	208/247.
<u>3756976</u>	Sep., 1973	Uraneck et al.	521/82.
<u>3898153</u>	Aug., 1975	Louder et al.	208/89.
<u>3945914</u>	Mar., 1976	Yoo et al.	208/240.
<u>4035474</u>	Jul., 1977	Kunkel et al.	423/574.
<u>4225417</u>	Sep., 1980	Nelson	208/89.
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<u>4456527</u>	Jun., 1984	Buss et al.	208/89.
<u>4534943</u>	Aug., 1985	Novak et al.	422/188.
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<u>4634518</u>	Jan., 1987	Buss et al.	208/138.
<u>5008096</u>	Apr. 16, 1991	Ringo, et al.	423/477
<u>5597539</u>	Jan. 28, 1997	Fakley, et al.	423/210
<u>5667760</u>	Sep. 16, 1997	Sweeney, et al.	423/224
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<u>0074894</u>	Mar., 1983	EP.
<u>3527110</u>	Feb., 1986	DE.
<u>2209386</u>	May., 1989	GB.

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Tsujihara et al., Sulfilimine I. Synthesis and Formation Mechanism, Bulletin of Chemical Society in Japan, vol. 42, 2631-2635(1969).

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Michael Reggelin, Cornelia Zur, Sulfoximines: Structures, Properties and Synthetic Applications, Synthesis 2000, No. 1, 1-64 ISSN 0039-7881 Thieme Stuttgart · New York.

Hirano M, Yakabe S, Clark J H and Morimoto T, *Oxidation of sulphides with sodium chlorite catalysed by manganese(III) acetylacetone in acetone in the presence of alumina* J Chem Soc Perkin 1, 1996, 2693-2698

L. H. Klemm, T.J.R. Weakly, and M. Moon, "X-Ray Crystallographic and NMR Structural Studies. Reactions of Thiophene Rings with Hypochlorite Reagents, "J. Heterocyclic Chem", Vol 36, 1077-1080 (1999).

Griggio, L., Electrochemical Reduction Mechanism of Sulfilimines: S,S-Diphenyl-N-p-Nitrobenzenesulfonylsulfilimine. *Electrochim. Acta*, 1982, 27, 749-753.

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I.W.J. Still and K. Turnbull; "Reduction of Sulfilimines to Sulfides with Phosphorus Pentasulfide"; *Synthesis*, 540-541 (1978).Paul et al., "Titrimetric Determination of Mercaptans with Chloramine-T," *Talanta*, 1975, 22(3), pp. 311-312, (Abstract).

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6. *Problem(s) solved: (Take as much space as needed to discuss your invention):

(a) Indicate what problems you are addressing. What are the obstacles, difficulties this area faces?

Contamination of hydrocarbon streams poses a problem for fuel technology and petrochemical processes. Breakthrough of sulfur from various sweetening processes result in catalyst poisoning, corrosion of tanks, ships, and pipelines, and cause the loss from flaring, reinjection, or discounted sales for off-spec hydrocarbons. In particular, dimethyl sulfide appears in some oil and gas fields, and cannot be removed by standard processes. Hydrogen sulfide and dialkyl disulfides also break through Amine and Merox processes, during process upsets, and result in off-spec hydrocarbons again causing flaring, reinjection, or discounted sales.

(b) What you have done to overcome the difficulties?

We have developed a new process which will remove mercaptans, thioethers, sulfides, disulfides and acid gasses (hydrogen sulfide, carbonyl sulfide, and carbon disulfide) from hydrocarbons.

(c) Describe the need for this invention in your field.

This new process is needed to safeguard our product quality and ensure the production of zero-sulfur hydrocarbons for fuel, fuel additives, fuel blending agents, petrochemicals, and other uses, and to prevent and alleviate the need for flaring, reinjection, or discounted sales.

7. *Detailed description of claims (limits, domain, ranges, "territory" of invention):

Describe the limitations, ranges, and any further clarifications regarding the application of the invention. Please take as much space as needed to address the topic (detailed information is required).

CLAIMS

We Claim:

- 1. A process for the removal of organosulfur compounds from a liquid hydrocarbon stream containing organosulfur compounds, said process comprising: exposing a liquid hydrocarbon stream comprising organosulfur compounds to a material comprising a reactive agent under conditions and time effective to permit said organosulfur compounds to react with said active agent to result in a resultant liquid hydrocarbon stream which is substantially devoid of sulfur.**
- 2. The process as defined in claim 1 is used for removing hydrogen sulfide, carbon disulfide, carbonyl sulfide, mercaptans, thioethers, sulfides, disulfides, and other sulfur compounds, from a hydrocarbon gas (NG) stream, a liquefied natural gas (LNG) stream, a natural gas liquids (NGL), and a liquid hydrocarbon stream, which comprises contacting said streams with an aqueous solution containing a mixture of agents which include sodium hypochlorite, hypochlorous acid, salt and acid forms of mixed oxides of chlorine, including chlorous acid, perchloric acid, chlorine dioxide, forms of cyanuric acid, {synonyms: *syn-triazine-2,4,6-triol*, *1,3,5-triazine-2,4,6(1H,3H,5H)-trione*, *syn-triazinetriol*, *2,4,6-trihydroxy-1,3,5-triazine*, *trihydroxycyanidine*, *tricyanic acid*, Molecular formula: C₃H₃N₃O₃ CAS No: 108-80-5 }, sodium trichloroisocyanuric acid, losantin (*technical grade calcium hypochlorite, CaOCl*), sodium hydroxide, (NaOH) and other components found in these agents.**
- 3. The process as described in claims 1 & 2 may be catalyzed by ferrous and nickelous sulfates, other salts of iron and nickel, other transition metal oxidation catalysts, and various forms of supported catalysts.**
- 4. The process as defined in claim 1, 2, & 3 wherein said process reduces sulfur content of resultant stream to less than 5 ppm.**
- 5. The process as defined in claim 1, 2, & 3 wherein said process reduces sulfur content of resultant stream to less than 1 ppm.**
- 6. The process as defined in claim 1, 2, & 3 wherein losantin (technical grade calcium hypochlorite), consists of calcium hypochlorite, calcium perchlorate, calcium hydroxide, calcium carbonate, calcium bicarbonate, calcium chlorate, or other calcium salts, and where the concentration of losantin (technical grade calcium hypochlorite), is varied from 0-35 weight %.**
- 7. The process as defined in claim 1, 2, & 3 wherein losantin (technical grade calcium hypochlorite), is of 25 % to 100 % purity of calcium hypochlorite.**

8. The process as defined in claim 1, 2, & 3 wherein sodium hypochlorite solutions of concentrations 0.1 to 35 % are used as the oxidizing-chlorinating agent, alone or in combination with other agents and catalysts.
9. The process as defined in claim 1, 2, & 3 wherein the cyanuric acid may be in the form of chloroisocyanurate, dichloroisocyanurate, trichloroisocyanurate, and it's sodium, potassium, calcium, or other alkaline or alkaline earth metal salts.
10. The process as defined in claim 1, 2, & 3 wherein the cyanuric acid may be in the form of mixtures of mono, di, and trichloro derivatives, and may be dissolved in the aqueous agent solution by adding caustic materials such as solids or solutions of various sodium, potassium, calcium hydroxides or hypochlorites.
11. The process as defined in claim 1, 2, & 3 wherein the sodium hydroxide or other caustic agent is effective to solubilize the various forms of cyanuric acid and it's chlorinated derivatives.
12. The process as defined in claim 1, 2, & 3 wherein the calcium hypochlorite or other bleaching agent is used to activate and chlorinate the forms of cyanuric acid.
13. The process as defined in claim 1, 2, & 3 wherein the various forms of cyanuric acid and it's chlorinated derivatives are effective to stabilize the hypochlorite forms in the agent solution.
14. The process as defined in claim 1, 2, & 3 wherein the agents defined are used in any combination, separately, individually, in various ratios, to their limits of solubility or stability, and where the agents are prepared beforehand and separately, or are generated in situ, or by reacting together the agents.
15. The process as defined in claim 1, 2, & 3 wherein the agents act together or separately to react with sulfur compounds, to oxidize, complex, bind, extract, chlorinate, aminate, form sulfonic acids, form sulfoxides, form sulfones, form sulfonium salts, form thiocarbamates, form sulfimines, form salts, form donor-acceptor complexes, form charge-transfer complexes, form aqueous soluble species, form insoluble species, or otherwise react, aggregate, and assemble in action to remove sulfur from the hydrocarbon streams.
16. The process as defined in claim 1, 2, & 3 wherein the hydrocarbon streams are contacted in a continuous process where the hydrocarbon stream is bubbled upward through a contactor containing the aqueous solution of the reactive extractive agents, or a static process where the hydrocarbon stream is stirred and agitated in a contactor containing the aqueous solution of the reactive extractive agents, or any process, wherein the hydrocarbon stream and the aqueous solution of the agent are first contacted for a suitable time period then allowed to separate, permitting and causing the removal of sulfur species from the hydrocarbon into the aqueous agent, and producing a hydrocarbon stream largely free of sulfur species, or at least much depleted in sulfur species.

17. The process as defined in claim 1, 2, & 3 where the reactions are catalyzed by the presence of ferrous sulfate, nickelous sulfate and other transition metal catalysts in their form as salts of chloride, hypochlorite, chlorate, carbonate, nitrate, sulfite, or any other anion suitable for the purpose. Other catalysts claimed are salts of molybdenum, cobalt, manganese, copper, chromium, tungsten, cerium, and other catalysts known to promote oxidation and chlorination of sulfur. The catalysts may be in the form of soluble or insoluble salts, supported on silica, alumina, zeolites, or other known catalyst supports.

8. Provide all test data, examples, and documents to support invention:

(Please use as much space as needed to document/prove that this invention works. IAM will not process this application without these documents)

(a) Show evidences to document that the invention actually works. Provide documents and present figures, pictures, tables, data etc. to make your point.

Saudi Aramco Lab Notebook Number 137-101-03 (Farhan Al-Shahrani) Pages 18-25. April-May-2003.

Saudi Aramco Lab Notebook Number 791(Gary D. Martinie) Pages 10-12. April-May-2003.

(b) Provide examples, if the invention can be scaled for appropriate field application and/or commercial use.

See Examples.

(c) Could others repeat this work based on the conditions or information provided? Describe how to repeat this work

Yes, just follow the examples.

(d) Any test results or experimental data presently available should be attached and described. Identify any reports or laboratory records in which the present invention is described (*IDs of record book and pages, indicate page numbers*). Attach copies of all records including photographs, drawings, sketches, illustrations, pictures, or animations depicting or describing the invention. Any future data, tests, or results should also be sent to IAM group.

Example 1, Extraction with Various Reagents

In this experiment, a stock solution of hydrocarbon containing butanes, pentanes, and hexanes was prepared, containing 82 mg/liter ethyl mercaptan, 84 mg/liter dimethyl sulfide, and 105 mg/liter dimethyl disulfide. Four extraction solutions were prepared as follows: Sodium Hypochlorite (5.25 %); Trichloroisocyanurate (1.70 %) and Sodium Hydroxide (2.00 %); Calcium Hypochlorite (1.50 %), and Sodium Hydroxide (1.59 %). A 10-ml sample of the stock solution was extracted separately by each of the reagent solutions for five minutes with intermittent shaking. The layers were allowed to settle, then an aliquot was withdrawn and analyzed by GC-SCD. The results appear in Table I. and indicate the efficiency of each reagent mixture.

Sodium Hypochlorite (5.25 %) was effective to remove more than 94 % of ethyl mercaptan and dimethyl sulfide, and removed more than 78 % of dimethyl disulfide. Less than one mg/liter of methyl ethyl disulfide, diethyldisulfide, and unknown disulfide were formed.

Trichloroisocyanurate (1.70 %) and Sodium Hydroxide (2.00 %) removed 87 % of ethyl mercaptan, 98 % of dimethyl sulfide, and removed only 20 % of dimethyl disulfide. Several mg/liter of methyl-ethyl disulfide, diethyldisulfide, and unknown disulfide were formed.

Calcium Hypochlorite (1.50 %) removed over 99 % of ethyl mercaptan and dimethyl sulfide, and removed only 40 % of dimethyl disulfide. About one mg/liter of methyl-ethyl disulfide and diethyldisulfide were formed.

Sodium Hydroxide (1.59 %) removed 98 % of the ethyl mercaptan, but only removed 38 % of the dimethyl sulfide and 12 % of the dimethyl disulfide. Several mg/liter of methyl-ethyl disulfide, diethyl disulfide, and unknown disulfide were formed.

The extractions were continued for one hour with intermittent shaking, then the layers were allowed to separate, and sample aliquots were withdrawn from each extraction hydrocarbon layer, and analyzed by GC-SCD. The results appear in Table II.

Sodium Hypochlorite (5.25 %) was effective to remove more than 96 % of ethyl mercaptan and dimethyl sulfide, and removed more than 92 % of dimethyl disulfide. Less than one mg/liter of methyl ethyl disulfide, diethyl disulfide, and unknown disulfide were formed.

Trichloroisocyanurate (1.70 %) and Sodium Hydroxide (2.00 %) removed 91 % of ethyl mercaptan, 98 % of dimethyl sulfide, and removed only 15 % of dimethyl disulfide. Several mg/liter of methyl-ethyl disulfide, diethyl disulfide, and unknown disulfide were formed.

Calcium Hypochlorite (1.50 %) removed over 99 % of ethyl mercaptan and dimethyl sulfide, and removed only 95 % of dimethyl disulfide. About one mg/liter of methyl-ethyl disulfide and diethyl disulfide were formed.

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Sodium Hydroxide (1.59 %) removed 98 % of the ethyl mercaptan, but only removed 50 % of the dimethyl sulfide and 26 % of the dimethyl disulfide. Several mg/liter of methyl-ethyl disulfide, diethyl disulfide, and unknown disulfide were formed.

STRICTLY CONFIDENTIAL**Example 2. Extraction with Sodium Hypochlorite and Nickel and Iron Catalysts**

A stock solution of 21 mg/liter ethyl mercaptan, 40 mg/liter dimethyl sulfide, and 71 mg/liter dimethyl disulfide in mixed hexanes was prepared. In this experiment the stock solution 10 ml was shaken with extraction solution of 10 ml 5.25 % NaOCl aqueous for five minutes in a 20 ml vial. The first sample was the stock solution. The second sample contained ferrous sulfate added at 500 mg/liter. The third sample contained nickelous sulfate at 500 mg/liter. The fourth sample contained 250 mg/liter ferrous sulfate and 250 mg/liter nickelous sulfate. The fifth sample contained only the NaOCl at 5.25 %. After shaking the samples for five minutes, the samples were allowed to separate and the top layer was sampled, added to the injection vial, and analyzed by GC-SCD. The samples were analyzed by GC-SCD with detection limit of 0.5 mg/liter sulfur. All concentrations are in mg/liter as sulfur. Used separately, the ferrous and nickelous catalysts are both effective at removing sulfur to less than 0.5 ppm, or 99.5 % removal. Mixed together, they are slightly less active, leaving a residue of 1 mg/liter from dimethyl disulfide. Sodium hypochlorite alone were very effective at removing all of the ethyl mercaptan and dimethyl sulfide, but only removed 53 % of the dimethyl disulfide.

EXPERIMENT MAY 4, 2003						
DMDS STK SLN = 71.21 MG/LITER SULFUR						
RESPONSE FACTOR= 50937/71.21=715.3						
	ETSH		DMS		DMDS	
Experiment	AREA	CONC	AREA	CONC	AREA	CONC
Retention Time	1.17		1.30		6.43	
Stock Solution	19403	27.1	28732	40.2	50937	71.2
NaOCl 5.25 % & Fe(SO ₄)	0.00	0.0	0.00	0.0	0	0.0
NaOCl 5.25 % & Ni(SO ₄)	0.00	0.0	0.00	0.0	0	0.0
NaOCl 5.25 % & Ni(SO ₄) & Fe(SO ₄)	0.00	0.0	0.00	0.0	731	1.0
NaOCl Extn 5.25 %	0.00	0.0	0.00	0.0	24011	33.6

TABLE I. CONCENTRATIONS FOUND AFTER FIVE MINUTE EXTRACTION

SAMPLE	ETSH A	DMS A	DMDS A	EMDS	UNKN	DEDS
Retention Time	1.42	1.57	7.21	9.93	10.68	12.75
Stock Soln Mg/Liter	82.2	83.9	104.6	0.0	0.0	0.0
NaOCl 5.25 %	4.6	5.0	22.3	0.2	0.0	0.2
TCI (1.70 %) & NaOH (2.00 %)	10.7	1.3	84.1	5.6	1.8	13.4
Ca(OCl) ₂ (1.50 %)	0.6	0.3	62.6	0.4	0.0	1.7
NaOH (1.59 %)	1.4	52.3	92.1	6.3	0.0	4.6

TABLE II. CONCENTRATIONS FOUND AFTER ONE HOUR EXTRACTION

SAMPLE	ETSH A	DMS A	DMDS A	EMDS	UNKN	DEDS
Retention Time	1.42	1.57	7.21	9.93	10.68	12.75
Stock Soln Mg/Liter	82.2	83.9	104.6			
NaOCl 5.25 %	3.4	2.9	8.0	0.2	0.0	0.2
TCI (1.70 %) & NaOH (2.00 %)	7.1	1.1	89.5	6.4	0.9	19.5
Ca(OCl) ₂ (1.50 %)	0.3	0.0	5.4	0.4	0.0	1.2
NaOH (1.59 %)	0.8	41.7	77.1	14.4	0.3	24.6

Example 3. Hypochlorite Extraction with Four Chambers Catalyzed by Nickel

In this Example, a solution of light hydrocarbons containing butanes, pentanes, and hexanes was treated with an extraction reagent using a contactor apparatus. The apparatus consisted of a fritt located at the bottom of the chamber which allowed the hydrocarbon to be pumped into the bottom of the reagent and slowly disperse upward through the reagent, collecting at the top of the chamber where it discharged out into a collection line. The chambers are filled with 250 ml of 5.25 weight % sodium hypochlorite, containing 500 mg/liter nickelous sulfate. The nickelous sulfate is present as a mostly insoluble dark blue solid, giving a slurry which is ebbulated by the action of the hydrocarbon passing through the aqueous layer. The apparatus is depicted in the attached figure. The light hydrocarbon contained 30 mg/liter methyl mercaptan, 32 mg/liter ethyl mercaptan, 27 mg/liter dimethyl sulfide, 29 mg/liter isopropyl mercaptan, and 148 mg/liter dimethyl disulfide.

Using an HPLC pump, the hydrocarbon mixture was pumped into the first reaction chamber at 10 ml/minute. After 30 minutes, a sample was collected and analyzed by GC-SCD.

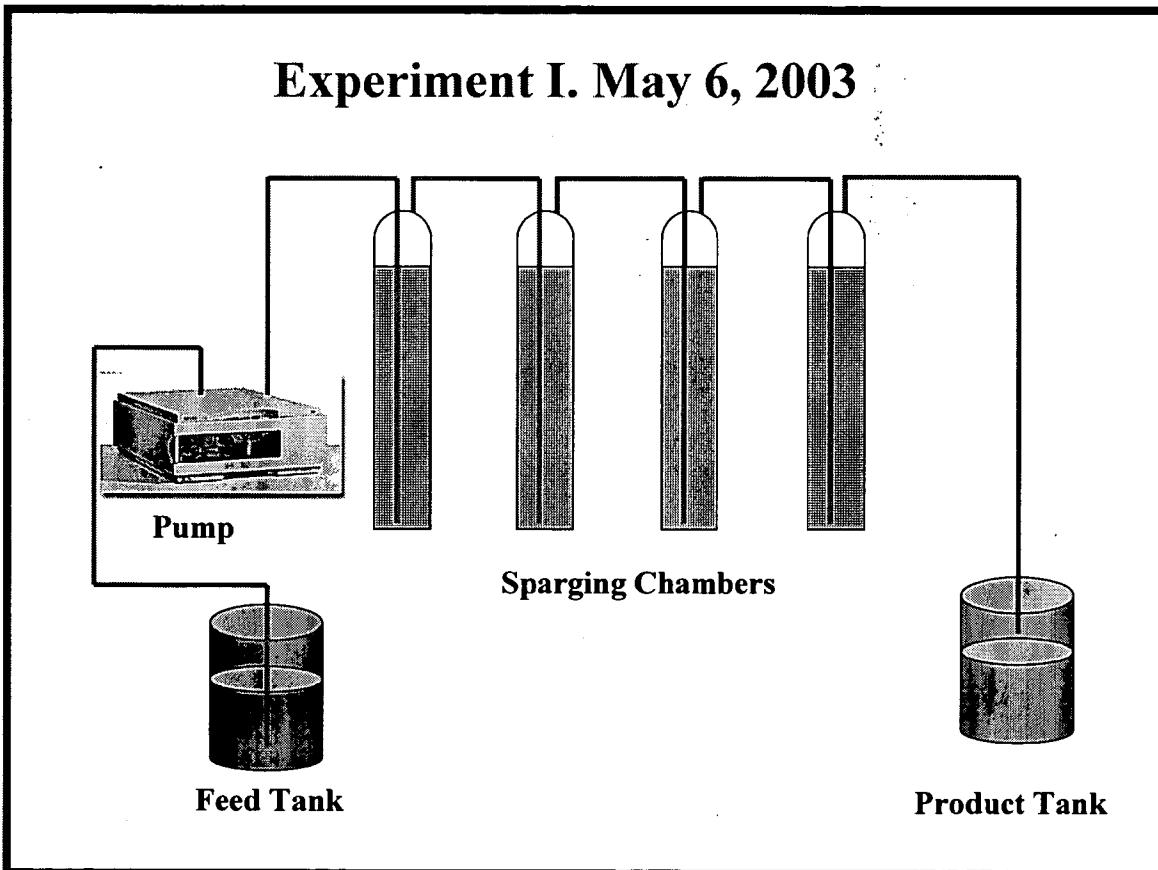
A second chamber was added to the assembled apparatus, and again, the hydrocarbon was pumped at 10 ml/minute. After 30 minutes, a sample was collected and analyzed by GC-SCD.

A third chamber was added to the assembled apparatus, and again, the hydrocarbon was pumped at 10 ml/minute. After 30 minutes, a sample was collected and analyzed by GC-SCD.

A fourth chamber was added to the assembled apparatus, and again, the hydrocarbon was pumped at 10 ml/minute. After 30 minutes, a sample was collected and analyzed by GC-SCD.

The data appear in the attached table, and show that sulfur components are reduced more after each chamber is added. After the third chamber, all of the sulfur compounds are eliminated, except dimethyl disulfide, which is reduced by 40 %. After the fourth chamber, all of the sulfur compounds are eliminated except dimethyl disulfide, which is reduced by 48 %.

MAY 6, 2003 EXPERIMENT I.					
Using One to Four Sparging Chambers					
	MG AS SULFUR PER LITER				
Sample	MTSH	ETSH	DMS	IPSH	DMDS
Retention Time	0.75	1.17	1.30	2.40	6.43
Stock Soln	30.0	32.3	26.8	28.6	147.9
First Chamber	1.1	1.8	0.3	123.8	123.8
Second Chamber	0.3	0.4	0.0	0.7	110.9
Third Chamber	0.0	0.0	0.0	0.0	89.0
Fourth Chamber	0.0	0.0	0.0	0.0	77.5



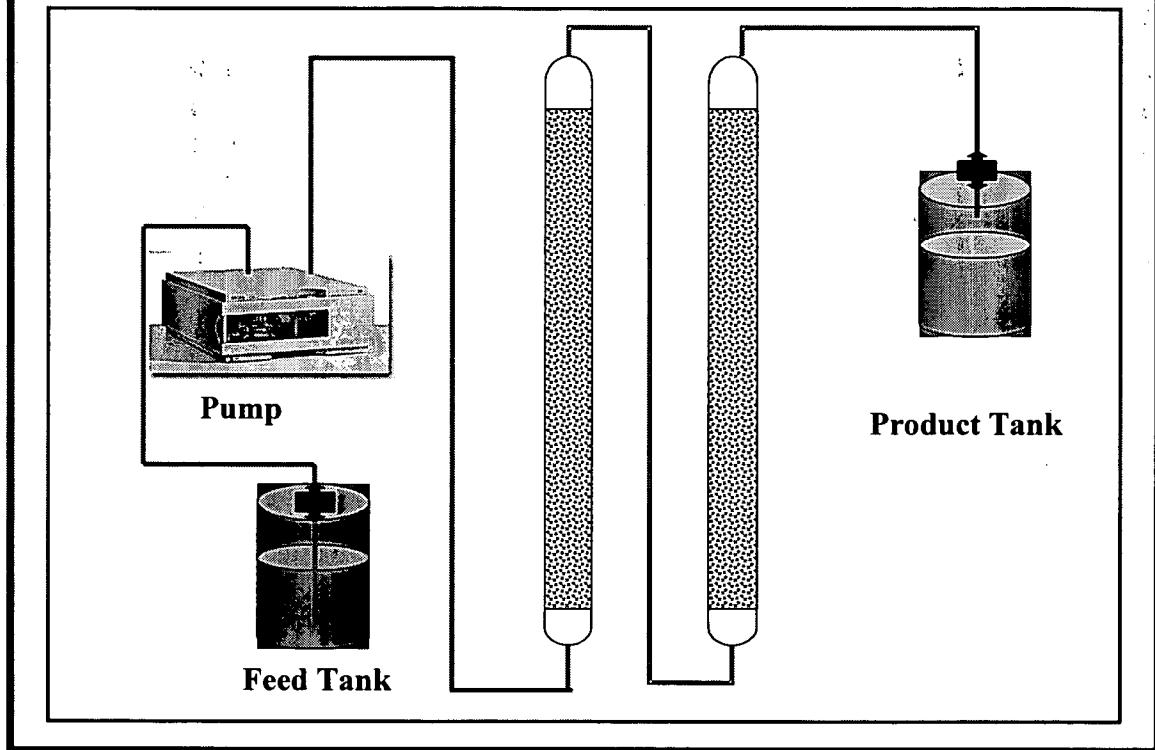
Example 4. Hypochlorite Extraction with Two Towers Catalyzed by Nickel

In this Example, a solution of light hydrocarbons containing butanes, pentanes, and hexanes was treated with an extraction reagent using an apparatus consisting of two 40 inch by two inch chromatography columns connected in series. The chromatography columns consist of a glass frit located at the bottom of the chamber which allowed the hydrocarbon to be pumped into the bottom of the reagent and slowly disperse upward through the reagent, collecting at the top of the chamber where it discharged out into a collection line. A stopcock is located below the glass frit which allows the apparatus to be filled without leaking, or drained, or flow to be interrupted. The chambers are filled with 600 ml each of 5.25 weight % sodium hypochlorite, containing 500 mg/liter nickelous sulfate. The nickelous sulfate is present as a mostly insoluble dark blue solid, giving a slurry which is ebullated by the action of the hydrocarbon passing through the aqueous layer. The apparatus is depicted in the attached figure. The light hydrocarbon contained 38 mg/liter methyl mercaptan, 34 mg/liter ethyl mercaptan, 27 mg/liter dimethyl sulfide, 25 mg/liter isopropyl mercaptan, and 148 mg/liter dimethyl disulfide.

Using an HPLC pump, the hydrocarbon mixture was pumped upward through the two chambers at 10 ml/minute. After the hydrocarbon first began to discharge from the second chamber, a sample was collected and analyzed by GC-SCD. Another sample was collected after 30 minutes, and another after 60 minutes. In the first sample, all the sulfur components were removed except dimethyl disulfide, which was reduced by more than 88 %. After 30 minutes, the sample showed all of the sulfur components had been removed except dimethyl disulfide, which was reduced by over 95 %. After 60 minutes, the sample showed all of the sulfur components had been removed except dimethyl disulfide, which was reduced by over 99 %. The data appears in the attached table.

MAY 6, 2003 EXPERIMENT II.					
Using Two 36 by Two Inch Chromatography Columns					
	MG AS SULFUR PER LITER				
Sample	MTSH	ETSH	DMS	IPSH	DMDS
Stock Soln	38.1	34.2	27.0	25.1	147.9
Time 0 Minutes	0.0	0.0	0.0	0.0	17.7
Time 30 Minutes	0.0	0.0	0.0	0.0	7.2
Time 60 Minutes	0.0	0.0	0.0	0.0	1.4

Experiment II. May 6, 2003



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Example 5. Extraction of Light Hydrocarbon with 15 Reagents

1	Blank	
2	New Chloramine T & 5 ml 5.25 % NaClO	100 ml DW
3	Old Chloramine T and 5 ml 5.25 % NaClO	100 ml DW
4	1.7 G Trichloroisocyanurate & 2.0 G NaOH	100 ml DW
5	2.0 G Isocyanuric Acid & 5.25 G NaOCl	100 ml DW
6	NaOH 1.6 G in 100 ml DW	100 ml DW
7	NaClO 5.25 G	100 ml DW
8	NaClO 5.25 G & 50 mg FeSO ₄	100 ml DW
9	NaClO 5.25 G & 50 mg NiSO ₄	100 ml DW
10	NaClO 5.25 G & 50 mg Each NiSO ₄ & FeSO ₄	100 ml DW
11	H ₂ O ₂ 30 G	100 ml DW
12	H ₂ O ₂ 30 G & 50 mg FeSO ₄	100 ml DW
13	H ₂ O ₂ 30 G & 50 mg NiSO ₄	100 ml DW
14	1.5 G Ca(ClO) ₂	100 ml DW
15	Distilled Water	100 ml DW

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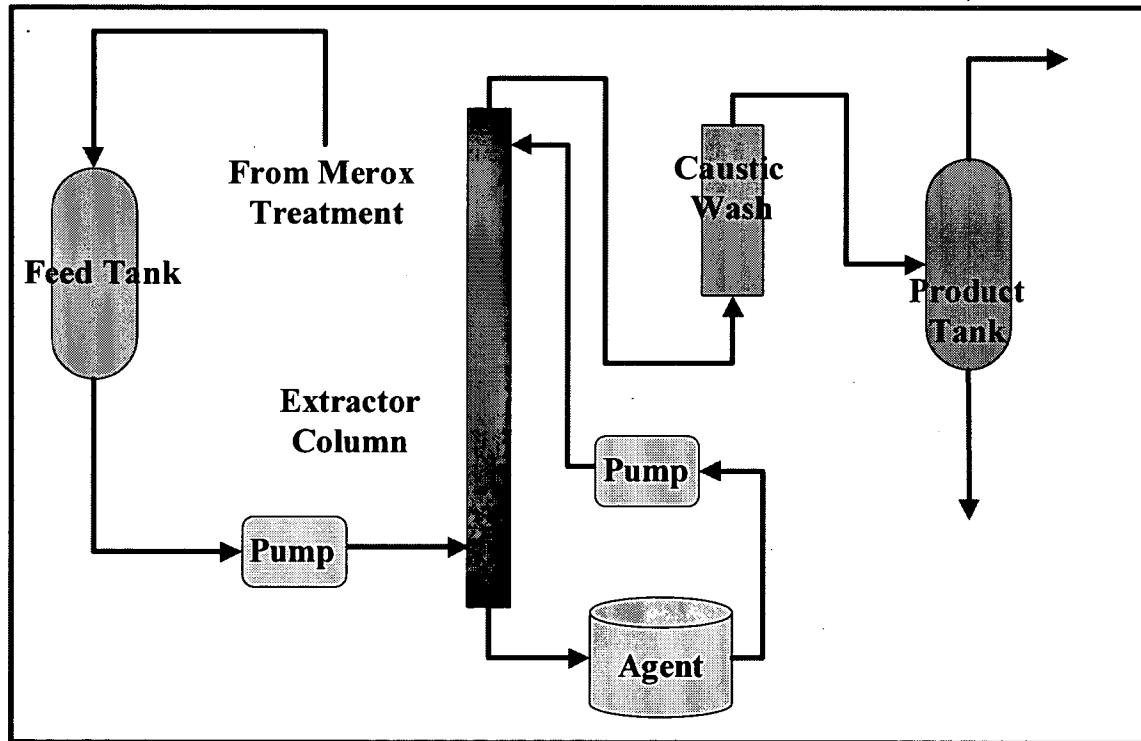
**Example 6. Extraction of Various Hydrocarbon Streams by optimized Reagent,
Including LPG, Pentanes, LSRN, SRN, Natural Gasoline, Condensate.**

Example 7. Description and Drawing of Butane Process

The process may be catalyzed by the presence of ferrous sulfate, nickelous sulfate and other transition metal catalysts in their form as salts of chloride, hypochlorite, chlorate, carbonate, nitrate, sulfite, or any other anion suitable for the purpose. Other catalysts claimed are salts of molybdenum, cobalt, manganese, copper, chromium, tungsten, cerium, and other catalysts known to promote oxidation and chlorination of sulfur. The catalysts may be in the form of soluble or insoluble salts, supported on silica, alumina, zeolites, or other known catalyst supports.

The process may be carried out as a batch process for example in a CSTR, or as a continuous process using countercurrent reactors, static aqueous phase contactors or scrubbers, or as a continuous process by passing the hydrocarbon stream through an aqueous agent containing the above listed chemicals. The process may be conducted at ambient temperature and pressure, or at elevated temperature and pressure. The process may include a post treatment to remove reagents and by products such as chloride, chlorine, oxygen, or chlorinated species. For example, a caustic wash after the reactor would be a sensible provision to remove residual chlorine, hypochlorite, or other undesirable species. Also a water wash may be a useful provision.

Butane Liquid-Liquid Extractor

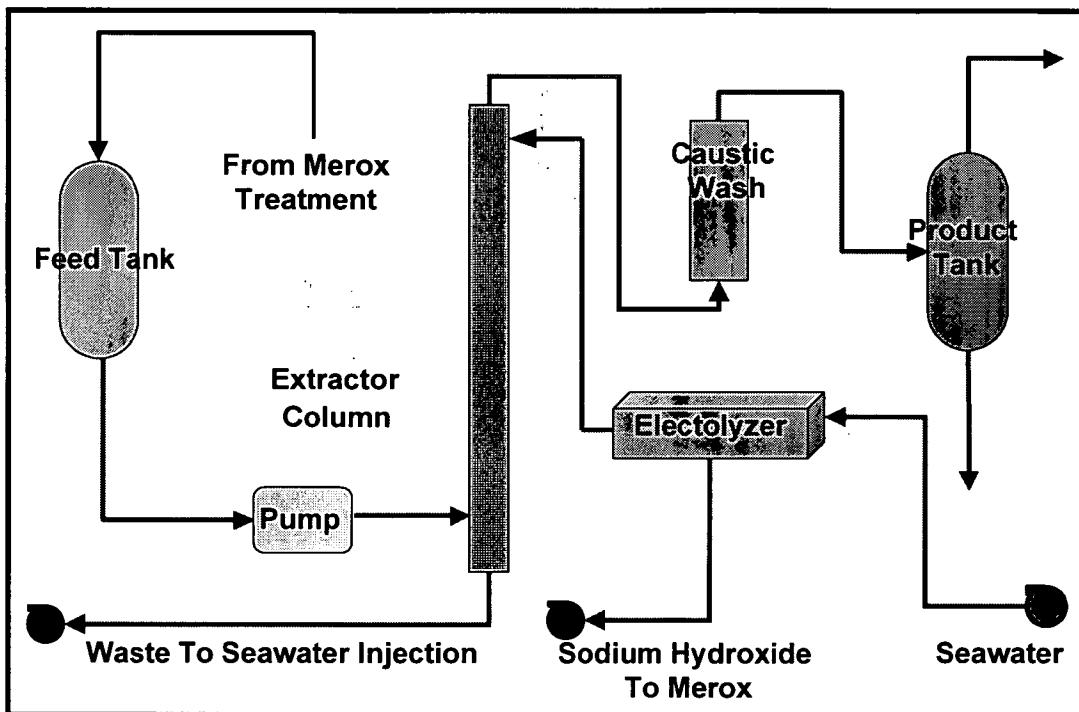


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Example 8. Example 7. Description and Drawing of Butane Process Using a Commercial Hypochlorite Generator

It may be desirable to utilize a commercial hypochlorite or hypochlorite generator instead of purchasing the hypochlorite or cyanurate chemicals. Commercial membrane electrolyzers are available to generate hypochlorous acid and sodium hydroxide by the electrolysis of seawater, and the byproduct sodium hydroxide can be used in refinery processes. The purge stream of spent hypochlorous acid from the extractor column may be used to treat seawater injected into the oil and gas fields.

Liquid-Liquid Extractor With Electrolyzer



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9. Abstract of the disclosure: Present an extended abstract

This process is a new technology designed to remove thioethers, mercaptans, disulfides, and other sulfur species from NGL, which are not removed by other processes such as Merox. This process uses a liquid-liquid extraction of the hydrocarbon liquid phase with an aqueous phase containing a complex mixture of chemicals. The process involves reactive extractive technology using a water soluble cocktail of low-cost industrial chemicals to react with thioethers and other sulfur species to form chlorosulfonium ions, sulfoxides, sulfones, sulfonic acids, sulfilimines, and other heavier, ionic, or water soluble species, and thereby separate and remove them from the hydrocarbon phase, trapping them in the aqueous phase.

A process for the removal of organosulfur compounds from a liquid hydrocarbon stream containing organosulfur compounds, said process comprising: exposing a liquid hydrocarbon stream comprising organosulfur compounds to a material comprising a reactive agent under conditions and time effective to permit said organosulfur compounds to react with said active agent to result in a resultant liquid hydrocarbon stream which is substantially devoid of sulfur.

The process as defined above is used for removing hydrogen sulfide, carbon disulfide, carbonyl sulfide, mercaptans, thioethers, sulfides, disulfides, and other sulfur compounds, from a hydrocarbon gas (NG) stream, a liquefied natural gas (LNG) stream, a natural gas liquids (NGL), and a liquid hydrocarbon stream, which comprises contacting said streams with an aqueous solution containing a mixture of agents which include forms of sodium hypochlorite, potassium hypochlorite, and calcium hypochlorite. Also effective are forms of hypochlorous acid, chlorous acid, perchloric acid, chlorine dioxide, mixed oxides of chlorine, and their salts. Also effective is cyanuric acid, {synonyms: *syn-triazine-2,4,6-triol*, *1,3,5-triazine-2,4,6(1H,3H,5H)-trione*, *syn-triazinetriol*, *tricyanic acid*, *2,4,6-trihydroxy-1,3,5-triazine*, *trihydroxycyanidine*, Molecular formula: C₃H₃N₃O₃ CAS No: 108-80-5 }, in it's chlorinated forms or in the presence of chlorinating agents. Also effective is chlorinated isocyanuric acid and it's salts of sodium, potassium, or calcium, including monochloro, dichloro, and trichloro isocyanurate. Also effective is Losantin (*technical grade calcium hypochlorite, CaOCl*), caustic soda, (*sodium hydroxide, NaOH*) and other components found in these agents.

The process may be catalyzed by the presence of ferrous sulfate, nickelous sulfate and other transition metal catalysts in their form as salts of chloride, hypochlorite, chlorate, carbonate, nitrate, sulfite, or any other anion suitable for the purpose. Other catalysts claimed are salts of molybdenum, cobalt, manganese, copper, chromium, tungsten, cerium, and other catalysts known to promote oxidation and chlorination of sulfur. The catalysts may be in the form of soluble or insoluble salts, supported on silica, alumina, zeolites, or other known catalyst supports.

The process may be carried out as a batch process for example in a CSTR, or as a continuous process using countercurrent reactors, static aqueous phase contactors or scrubbers, or as a continuous process by passing the hydrocarbon stream through an

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aqueous agent containing the above listed chemicals. The process may be conducted at ambient temperature and pressure, or at elevated temperature and pressure. The process may include a post treatment to remove reagents and by products such as chloride, chlorine, oxygen, or chlorinated species. For example, a caustic wash after the reactor would be a sensible provision to remove residual chlorine, hypochlorite, or other undesirable species. Also a water wash may be a useful provision.

It may be desirable to utilize a commercial hypochlorite or hypochlorite generator instead of purchasing the hypochlorite or cyanurate chemicals. Commercial membrane electrolyzers are available to generate hypochlorous acid and sodium hydroxide by the electrolysis of seawater, and the byproduct sodium hydroxide can be used in refinery processes.

10. Benefit of your invention to the Saudi Aramco

Invention title: Reactive Extractive Removal of Thioethers, Mercaptans, Disulfides, and Other Sulfur Species from Natural Gas, Liquefied Natural Gas, Natural Gas Liquids, Light Straight Run Naphtha, Straight Run Naphtha, Natural Gasoline, Hydrocracker Naphtha, Coker Naphtha, and Light Petroleum Fractions.

Please categorize this invention and tell us why you view this way. Base your decision on the following: strategic importance or operational impact, safety, security or environmental issues or any other considerations.

1. Utility of your Invention (check one or more below)

This invention will be **immediately** applied by Saudi Aramco (explain)

Highly **relevant** important work and must receive immediate attention. This work is of highest importance for my business unit. (explain)

Related to company's core business areas (explain).

A patent should be filed but work is not related to company's core business. However, the work contributes to the company's **intellectual assets** (IP).

2. Use of the Invention: When and where this invention will be applied within Saudi Aramco? (Check one).

1	<input type="checkbox"/>	Immediately (0-3 months) where? _____
2	<input checked="" type="checkbox"/>	3 months – 2 years where? Juaymah Gas Plant
3	<input checked="" type="checkbox"/>	2 – 5 years where? Rabigh , Yanbu, Ras Tanura Refineries
4	<input checked="" type="checkbox"/>	5+ years where? Yanbu Gas Plants